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Determination of Nonmethane Organic Carbon (NMOC) by Cryogenic Preconcentration and Flame Ionization Detection

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16. ABSTRACT

A variety of photochemical dispersion models have been developed to describe the quantitative relationships between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone. An important application of such models is to determine the degree of control of such organic compounds that is necessary to achieve compliance with ambient air quality standards for ozone.

The method described can be used to obtain the requisite upwind NMOC measurements. This method is sort of acompromise between the continuous and GC methods. It combines cryogenic concentrations techniques used in the GC method for high sensitivity with the simple flame ionization detector (FID) for total NMOC measurements without the complex GC system necessary for species resolution. And because of the use of helium carrier gas, the FID has less response variation to various organic compounds than a conventional NMOC analyzer with direct air infusion.

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DETERMINATION OF NONMETHANE ORGANIC CARBON (NMOC) BY CRYOGENIC PRECONCENTRATION AND FLAME IONIZATION DETECTION

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INTRODUCTION

A variety of photochemical dispersion models have been developed to describe the quantitative relationships between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone.[1] An important application of such models is to determine the degree of control of such organic compounds that is necessary in a particular area to achieve compliance with applicable ambient air quality standards for ozone.[1,2] For this purpose, the models require input of nonmethane organic compounds (NMOC) concentration data.

The more elaborate theoretical models generally require detailed organic species data.[2] Such species data must be obtained by analysis of air samples using a sophisticated, multicomponent gas chromatographic (GC) analysis system.[2,3] Simpler empirical models such as the Empirical Kinetic Modeling Approach (EKMA) require only total NMOC concentration data, specifically the average total NMOC concentrations from 6 a.m. to 9 a.m. daily.[2]

For many EKMA applications, NMOC measurements are required at urban, center-city-type sites.[2] The moderately high NMOC concentrations typically found at such urban sites can be adequately measured by commercially available continuous (or semicontinuous) NMOC analyzers.[2,4] However, if transport of precursors into an area is to be considered, then NMOC measurements upwind of the area are necessary.[1] Upwind NMOC concentrations are likely to be very low (less than a few tenths of 1 ppm) and therefore may not be adequately measured by conventional NMOC anlayzers.[2,4] NMOC GC species measurements can be used by summing the various components

to obtain a total NMOC concentration.[2] But for EKMA, the species data are not needed, and the cost of species analysis is very high.

The method described herein can be used instead to obtain the requisite upwind NMOC measurements.[5,6] This method is a sort of compromise between the continuous and GC methods mentioned above. It combines the cryogenic concentration technique used in the GC method for high sensitivity with the simple flame ionization detector (FID) for total NMOC measurements without the complex GC system necessary for species resolution. And because of the use of helium carrier gas, the FID has less response variation to various organic compounds than a conventional NMOC analyzer with direct air injection.

This method can be used either for direct, in situ ambient measurements or for analysis of integrated samples from a sample bag or canister. Making direct measurements at the monitoring site avoids the potential sample loss or contamination problems inherent with the use of bags or canisters. However, the analyst must be present during the 6 to 9 a.m. period, and repeated measurements must be taken to obtain the 6 to 9 a.m. average NMOC concentration. A separate analytical system and analyst (or a conventional NMOC analyzer) is needed for each monitoring site.

The use of sample bags or canisters allows the collection of integrated air samples over the 6 to 9 a.m. period by automated samplers at unattended monitoring sites. One analytical system can then analyze the samples from several monitoring sites. But degradation or contamination of the air samples by the bag or canister may be a significant problem.

One possible compromise is to locate the analytical system at the upwind site for direct measurements of the low upwind NMOC concentrations, with integrated bag or canister samples collected at the urban monitoring sites. Direct measurements are carried out during the 6 to 9 a.m. period after which the bag or canister samples from the urban site are brought to the upwind site for subsequent analysis. The higher concentrations at the urban sites will minimize the effect of losses or contamination of the bag or canister samples, while the low, upwind concentrations are measured directly. All measurements can be made with a single analytical system.

DETERMINATION OF NONMETHANE ORGANIC CARBON (NMOC) BY CRYOGENIC PRECONCENTRATION AND FLAME IONIZATION DETECTION

1. APPLICABILITY

This method is applicable to measurements of total gaseous nonmethane organic carbon (NMOC) concentrations in the atmosphere for use with atmospheric photochemical dispersion models such as EKMA.[1] Measurements may be obtained either in situ, or by subsequent analysis of integrated air samples collected over a fixed time period such as the 3-hour (6 to 9 a.m.) measurements specified for EKMA. Collection of integrated samples also allows for remote analysis of samples from multiple sites. The high sensitivity and low detection limit of the method make it suitable for upwind measurements, while the wide dynamic range allows analysis of urban air samples as well.

2. PRINCIPLE

An air sample is taken either directly from the ambient air at the monitoring site or from a sample bag or canister filled previously at the site. A fixed-volume portion of the sample is drawn at a low flow rate through a tubular trap cooled to approximately -185° C. This temperature is such that most, if not all, organic compounds in the sample other than methane are trapped (either via condensation or adsorption) in the tube, while methane, nitrogen, oxygen, etc., pass on through. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and analytical phases.

After the fixed volume air sample has passed through the trap, a flow of helium is flushed through the trap and into a commercially avail-

able FID analyzer that is modified to operate with a helium carrier. When the residual methane and oxygen have been cleared from the trap and the FID baseline becomes steady, the temperature of the trap is raised to approximately 70°-80° C. The organic compounds collected in the trap revolatilize and are carried into the FID, resulting in a response peak or peaks on a chart recorder connected to the FID analyzer output. The area of the peak is integrated, and the integrated value is translated to concentration units via a previously obtained calibration curve relating integrated reading with known concentrations of propane.

The cryogenic trap simultaneously concentrates the nonmethane organic compounds and separates and removes methane. Thus the technique is both direct reading for NMOC and more sensitive than conventional NMOC analyzers. Also, operation of the FID analyzer with a helium carrier results in less response variation to different organic compounds than is observed with conventional NMOC analyzers having direct air injection. Quantitative trapping has been shown for most compounds tested.[5]

3. PRECISION AND ACCURACY

Precision has been found to be within ±5 percent for standard gas calibrations and generally ±10 percent for ambient samples. Accuracy for ambient air samples has been determined to be ±15 percent by comparison with manual GC analysis. Experimental results also show no significant effect of humidity over a wide range of concentrations.

4. APPARATUS

The following components and materials are required or recommended. Sources for the more specialized components are given in Appendix A. An overall schematic diagram of the analytical system is shown in Figure 1,

and a suggested system for collecting ambient samples in canisters or bags is shown in Figure 2.

4.1 Direct Sampling

4.1.1 Sample manifold or sample inlet line. To bring air sample into the analytical system.

4.1.2 Vacuum pump. Inexpensive vacuum pump or blower to draw air sample through sample manifold or inlet line with a low residence time.

4.2 Sample Collection in Pressurized Canisters

4.2.1 Sample canisters. Stainless steel pressure vessels of 4- to 6-L volume having electropolished interior and integral, leak-free shut-off valve (see Appendix). Each canister should have a unique identification number.

4.2.2 Sample pump. Metal Bellows model MB-151 or equivalent, capable of 2 atmospheres (30 psig) output pressure. Pump must be clean and uncontaminated by oil or organic compounds.

4.2.3 Auxiliary pump. Inexpensive vacuum pump to draw air sample through inlet line to sample pump with a low residence time.

4.2.4 Pressure gauge. 0-200 kPa (0-30 psig).

4.2.3 Shut-off valve.

4.2.6 Stainless steel capillary. 0.025 cm i.d., length as required (see Section 6.2).

4.2.7 Vacuum pump. Capable of evacuating the sample canisters to an absolute pressure of 10^{-3} mm Hg.

4.2.8 Vacuum manifold. A stainless steel manifold with connections for several canisters to be simultaneously cleaned.

4.2.9 Bellows valve. A low leakage vacuum valve placed in-line between the vacuum pump and the vacuum manifold.

4.2.10 Vacuum gauge. Capable of measuring the vacuum of the vacuum manifold to an absolute pressure of 10^{-3} mm Hg.

4.2.11 Insulated heater box. Capable of heating stainless steel canisters to 150° C for cleanup.

4.2.12 Needle valve. Fine metering valve to adjust flow of sample from canister during analysis.

4.2.13 Cryogenic trap. Cooled with liquid nitrogen to prevent contamination from back diffusion of oil from the vacuum pump.

4.3 Sample Collection in Bags

4.3.1 Sampling bag. Tedlar, 8- to 12-L capacity, with shut-off valve.

4.3.2 Sample pump. Noncontaminating, to fill bags over required time period. System described for canisters may be used (without the pressure gauge).

4.3.3 Vacuum pump. Inexpensive type to evacuate bags prior to use.

4.4 Analytical System

4.4.1 FID TOC analyzer. Beckman model 400 Hydrocarbon Analyzer, modified for helium carrier input as described in Section 6.4.8, or equivalent.

4.4.2 Six-port chromatographic valve. Valco model 9110, or equivalent.

4.4.3 Trap. Fabricated from a 120-cm length of 0.3175 cm (1/8 in.) o.d., 0.21 cm i.d. chromatographic grade stainless steel tubing to the dimensions shown in Figure 3.

4.4.4 High pressure regulator. Standard, two-stage cylinder pressure regulator, with pressure gauges, for helium cylinder.

4.4.5 Low pressure regulator. Single stage with pressure gauge, to maintain constant helium carrier gas flow rate.

4.4.6 Needle valve. Fine metering valve to adjust sample flow rate through trap.

4.4.7 Cryogenic Dewars (2). Sized to contain submerged portion of trap, to hold liquid cryogen and hot water.

4.4.8 Absolute pressure gauge. 0-200 torr, Wallace-Tiernan model 61D-ID-0200, or equivalent.

4.4.9 Vacuum reservoir. Vacuum tank of about 2-L capacity.

4.4.10 Gas purifiers. Gas scrubbers containing Drierite or silica gel and 5A molecular sieve to remove moisture and organic impurities in the helium carrier gas, air, and hydrogen.

4.4.11 Shut-off valves (2). Leak free.

4.4.12 Vacuum pump. Capable of evacuating the vacuum reservoir to a pressure of 10 torr.

4.4.13 Chart recorder. Of suitable input voltage and chart speed to record graphic record of peaks from the FID analyzer.

4.4.14 Integrator. Or integrating chart recorder in lieu of 4.4.13, compatible with FID analyzer output and suitable to integrate peak areas.

4.5 Other Materials

4.5.1 Various connecting tubing and plumbing fittings. All such items in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert material.

4.5.2 Various mechanical mounting fixtures as necessary.

5. SUPPLIES

5.1 Helium. Cylinder of zero-grade helium containing less than 0.5 ppmC hydrocarbons.

5.2 Combustion air. Cylinder of zero-grade air containing less than 0.5 ppm hydrocarbons.

5.3 Hydrogen. Cylinder of pure hydrogen containing less than 0.5 ppmC hydrocarbons.

5.4 Propane calibration standard. Cylinder containing 5 to 100 ppm propane in air. Cylinder assay should be traceable to a National Bureau of Standards (NBS) propane in air Standard Reference Material (SRM) or a commercially available Certified Reference Material (CRM).

5.5 Zero air. Air containing less than 0.01 ppmC hydrocarbons. May be obtained from a cylinder of zero-grade compressed air scrubbed with Drierite or silica gel and 5A molecular sieve or activated charcoal or by catalytic cleanup of ambient air.

5.6 Liquid oxygen or liquid argon.

5.7 Hot water, 70°-80° C.

6. SYSTEM DESCRIPTION

6.1 Direct Sampling

A portion of the air flowing in the inlet manifold or inlet line is removed with a TEE connection and delivered directly to port five of the six-port valve. This connecting line should be kept as short as possible to minimize its dead volume. The NMOC measurement will represent the average NMOC concentration in the air sample during the trapping phase

(about 10-20 minutes). Direct sampling avoids potential sample degradation or contamination from sample collection containers.

6.2 Sample Collection in Pressurized Canisters

Collection of ambient air samples in pressurized canisters provides a number of advantages, including (1) integration of ambient samples over a time period, e.g., 3 hours; (2) remote sampling and central analysis; (3) storage and shipping of samples; (4) unattended sample collection; (5) analysis of samples from multiple sites; and (6) collection of replicate samples for statistical analysis. However, great care must be exercised in selecting, cleaning, and handling the canisters and sampling apparatus to avoid losses or contamination of the samples.

Figure 2 shows a schematic of a recommended sample collection system. The small auxiliary pump purges the inlet manifold or lines with a flow of several liters/minute to minimize the sample residence time. The larger Metal Bellows pump (MB-151) takes a small portion of this sample stream and pressurizes it to fill the canisters. Both pumps should be shockmounted to a plywood base, which should also have rubber feet, to minimize vibration.

The capillary connecting the outlet of the Metal Bellows pump to the canisters is used to limit the flow into the canisters and must be cut to a length that provides the desired flow rate. This flow rate is chosen so that the canisters are pressurized to at least 1 atmosphere above ambient pressure (2 atmospheres absolute pressure) over the desired sample period. The flow rate can be calculated by

$$F = \frac{P\ V\ N}{T \times 60} \qquad (1)$$

where

F = Flow rate, cm^3/min

P = Final canister pressure, atmospheres absolute

V = Volume of the canister, cm^3

N = Number of canisters

T = Sample period, hours.

For example, if two 4-L canisters are to be filled to 2 atmospheres (15 psig) in 3 hours,

$$F = \frac{2 \times 4000 \times 2}{3 \times 60} = 89 \ cm^3/min.$$

The canisters are originally evacuated, and once they are filled to above atmospheric pressure (about half the sample period), then pressure can be monitored with the pressure gauge. The connecting lines between the capillary and the canisters should be as short as possible to minimize their volume. Be sure the pump outlet pressure is at least 1 atmosphere higher than the final canister pressure so that the flow rate remains constant over the entire sampling period.

At least two canisters should be filled simultaneously in case one is contaminated or lost by leakage. Three or more canisters filled simultaneously would offer even greater protection, and replicate samples provide useful quality control information.

Prior to field use, each sampling system should be tested for pump contamination (see Section 7.2), leaks, and proper flow rate. The plumbing on the outlet side of the Metal Bellows pump can be checked for leaks by shutting off the canister valves, pressurizing the system, and checking fittings, etc., with a nonhydrocarbon-based leak detector fluid. The

MB-151 pump should also be leak checked by plugging its outlet and ensuring that there is no flow into its inlet side using a soap film flowmeter. The canisters must be cleaned and checked for contamination before use (see Section 7.1).

During analysis, pressurized canisters are connected to port five of the six-port valve via a needle value (V4) and vent as shown in Figure 1. The needle valve reduces the canister pressure and adjusts the canister flow rate to a value slightly higher than the trap flow rate set by valve V3. The excess flow exhausts through the vent, which assures that the sample air flowing through the trap is at atmospheric pressure. The vent is submerged in water so that the escaping bubbles provide a visual indication of vent flow and assist in adjusting valve V4.

6.3 Sample Collection in Bags

Sample bags are simpler, more readily available, and less expensive than canisters. But bags cannot be cleaned with heat and vacuum as canisters can, and contamination from bag outgassing or permeation through the bag may be a significant problem. Bag samples must be analyzed within 3 hours and must be protected from heat and sunlight. Containing the sample bags in cardboard boxes is recommended.[6]

6.4 Analytical System

6.4.1 Sample volume metering system. The vacuum reservoir and pressure gauge (see Figure 1) are used to meter precisely repeatable volumes of sample air through the cryogenic trap to concentrate the sample. With valve V2 closed and valve V1 open, the reservoir is first evacuated with the vacuum pump. Then V1 is closed and V2 is opened to allow a fixed volume of

air to enter the reservoir via the trap and six-port valve. The volume of air sampled is determined by the pressure rise measured by the pressure gauge. This volume can be calculated by

$$V_s = \frac{\Delta P \; V_r}{P_s} \qquad (2)$$

where

V_s = Volume of air sampled, standard cm^3

ΔP = Pressure difference measured by gauge, torr

V_r = Volume of vacuum reservoir

P_s = Standard pressure (760 torr).

For example, with a vacuum reservoir of 1700 cm^3 and a pressure charge of 180 torr (20 to 200), the volume sampled would be 403 cm^3. The actual reservoir volume is noncritical, since it will be constant throughout calibration and sample analysis, but changing the volume of the sample will change the sensitivity of the method. Sample volumes of 200 cm^3 to 500 cm^3 appear to be appropriate for typical ambient NMOC concentrations. If the response peak obtained for a 500-cm^3 sample turns out to be outside the calibration range or off scale, a second analysis of a 250-cm^3 sample can be carried out.

6.4.2 Trap. The trap should be carefully constructed from a single piece of tubing in the shape shown in Figure 3. The coil must fit conveniently into the Dewar flasks (Section 4.4.7), and the arms must be of an appropriate length to allow the coil to be completely submerged below the level of liquid cryogen in the

Dewar. The trap should connect directly to the six-port valve to minimize line length between the trap and the FID analyzer. Also, it must be mounted to allow the Dewars to be conveniently slipped on and off the trap.

6.4.3 Liquid cryogen. Either liquid oxygen (bp -183.0° C) or liquid argon (bp -185.7° C) may be used for the cryogen; experiments have shown no difference in trapping efficiency between the two cryogenic liquids.[5] However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen (bp -195° C) should not be used as the cryogen as it causes condensation of oxygen and methane in the trap. The level of the liquid seems to be important, so it should be constant at a point that completely covers the trap coils.

6.4.4 Heat source. To facilitate integration of the NMOC response peak, a hot bath is used to volatilize the concentrated NMOC so it is seen by the FID as one (or only a few) sharp and easily integrated peaks. Without using hot water, components of the sample "fractionally distill" off the trap as it warms up to room temperature and a series of small, hard-to-integrate peaks result. The water should be heated to above 75° C but not to boiling (100° C). A simple heating source is an electrical immersion heater, which readily heats about 1 L of water to 75° to 85° C.

6.4.5 Carrier gas. Helium is used to purge residual air and methane from the trap at the conclusion of the sampling phase, and to carry the revolatilized NMOC from the trap into the FID. The

helium flow of 76 cm^3/min is determined by the sample capillary in the FID analyzer and the pressure setting of the single-stage regulator. This single-stage regulator may not be necessary, but it is recommended to regulate helium pressure better than the two-stage cylinder regulator. When used, the secondary stage of the two-stage regulator must be set at a pressure higher than the pressure setting of the single-stage regulator.

6.4.6 Gas purifiers. Carrier helium, burner air, and burner hydrogen should all be passed through Drierite/Molecular Sieve 5A gas purifiers to remove water, oil, and organics from these support gases. If commercial "zero-air" is used for dilution purposes, it too should be passed through a scrubber, and if possible, an MSA Model 458060 (or equivalent) catalytic oxidizer to remove contaminant hydrocarbons that are frequently found in commercial zero-air.

6.4.7 Construction. The configuration of analytical components shown in Figure 4 has all the hardware (except the FID analyzer) mounted on an aluminum panel that fits into an aluminum suitcase with outside dimensions 45.7 × 44 × 30.5 cm. By using aluminum angle around three sides of the panel, the analytical assembly can be attached directly to the angle and easily removed from the case.

All tubing used for the system should be 0.3175 cm (1/8 in) stainless steel connected with stainless steel fittings. Connections for vacuum and helium carrier gas are made through bulkhead fittings on the panel. Other connections are made

directly to the six-port valve. The stainless steel line to the analyzer from the six-port valve should be kept as short as possible to avoid losses due to cooling, adsorption, and spreading of the sample peak. The trap is shown connected directly to the valve, and the entire valve assembly is offset 5 cm from the panel to provide clearance for the Dewars.

After assembly, the system should be pressurized to about 80 psig (550 kPa) and checked for leaks. During this procedure, disconnect the absolute pressure gauge and cap the line to prevent damage to the gauge. If the system is leak free, depressurize the system and reconnect the gauge.

6.4.8 FID analyzer. The Beckman 400 Total Hydrocarbon Analyzer must be modified as shown in Figure 5. The physical modification consists of disconnecting the original sample bypass line leading to the back-pressure regulator. The point at which this line was connected to a TEE fitting near the input port is capped off. Thus the entire sample input is directed through the sample capillary to the FID. The normal burner air and hydrogen flow rates are also changed to 650 cm^3/min for burner air and 45 cm^3/min for hydrogen. The use of these flow rates and the helium carrier instead of air carrier results in more uniform FID response to various hydrocarbon compounds.

6.4.9 Linearity. Response has been shown to be linear from 150 ppbC to 5000 ppbC with slightly nonlinear response below 150 ppbC.[5]

6.4.10 Range. The Beckman analyzer provides both a front panel "range" (attenuator) control and an internal full-scale output

voltage selector. An appropriate combination should be chosen so that an adequate output level for accurate integration is obtained down to the detection limit, yet the electrometer of the analyzer should not be driven into saturation at the upper end of the calibration. Saturation of the electrometer is indicated by a front panel meter reading of over 100 percent. Additional adjustment of range and sensitivity can be provided by the sample volume used, as discussed in Section 6.4.1.

6.4.11 Integrator. The integrator must be electrically compatible with the output signal of the FID analyzer so that sufficient resolution is available at low concentrations without overranging on high concentrations. If both an integrator and a separate chart recorder are used, care must be exercised to be sure they don't interfere with each other electrically. Range selector controls on both the integrator and the FID analyzer may not provide accurate range ratios, so individual calibration curves should be prepared for each range to be used.

Setting the zero-baseline of the integrator is very important to the accuracy of the method. Consult the integrator instruction manual for proper setting of the baseline. In particular, a negative FID response may occur if the trap is heated too rapidly during analysis. Some automated integrators may thus select an incorrect zero baseline. It may be necessary to use an integrator whose zero baseline can be set manually.

7. PROCEDURE

7.1 Recommended Procedure for Canister Decontamination

7.1.1 Connect canisters to the vacuum manifold in the heated box as shown in Figure 6. Close the lid and heat to 150° C.

7.1.2 Open the canister shut-off valves and evacuate to 0.5 mm Hg, using a liquid-nitrogen-cooled trap on the vacuum line to eliminate back-diffusion of hydrocarbons and oil from the vacuum pump.

7.1.3 Close bellows valve V5 and shut-off valve V7. Open valve V6 to pressurize canisters to 40 to 60 psig (300 to 400 kPa).

7.1.4 Close valve V6 and allow the canisters to remain pressurized for 15 to 20 minutes.

7.1.5 Open valve V5 and evacuate the canisters to 0.5 mm Hg. Open valve V7 only after the manifold pressure is below ambient pressure to monitor the vacuum.

7.1.6 Allow the canisters to remain evacuated for 10 to 15 minutes. Then close valves V5 and V7.

7.1.7 Repeat steps 7.1.3 to 7.1.6 two times.

7.1.8 Fill canisters with zero air and analyze them for contamination as a blank check of the cleanup system and procedures.

7.1.9 Reevacuate the canister after the analysis.

7.1.10 Attach a paper tag to each canister for field notes and take the container to the site.

7.2 Procedure for Collection of Samples in Pressurized Canisters

7.2.1 Leak-test all canisters by pressurization to 60 psig (400 kPa) with zero air and immersion in water.

7.2.2 Clean the canisters according to the procedure in Section 7.1. Any canisters that cannot be cleaned by repeated cleaning should not be used.

7.2.3 Check the pump for contamination by filling two evacuated, cleaned canisters with zero air and analyzing them.

7.2.4 Assemble a sample collection system such as the one shown in Figure 2. All canisters used should be cleaned and checked for contamination according to Section 7.1.

7.2.5 Turn on pumps and allow them to warm up for 15 minutes. After warming up, check the flow rates (see Section 6.2) with a soap film flowmeter; then loosely attach the fittings to the canisters for at least 1 minute. Leave the canister valves and the gauge shut-off valve closed.

7.2.6 Without turning off the pumps, tighten the fittings, then open the canister shut-off valves.

7.2.7 The canisters will fill slowly over the selected period at the predetermined flow rate. At the end of the sample period, measure the pressure with the pressure gauge connected at the union cross to ensure that the canisters have been pressurized to 2 atmospheres.

7.2.8 Close canister valves and tighten. Remove them from the pump setup and recheck the sample flow rate to see if it has changed from the initial flow rate. Then turn off the pumps.

7.2.9 The identification tags on the sample canisters should be filled out as necessary. Bring the canisters to the analytical system for analysis.

7.2.10 Complete records of the sampling should be entered in a laboratory notebook. The sampling operator should be alerted to take note of any activities in the area that may affect the sample contents.

7.3 Procedure for Cleaning Sample Bags

7.3.1 Check bag for absence of leaks.

7.3.2 Evacuate bag and fill with zero air three times.

7.3.3 Let bag stand for 1 hour filled with zero air.

7.3.4 Analyze the zero air from the bag to see if contamination is insignificant.

7.3.5 Evacuate the bag and take it to the sampling site.

7.4 Procedure for Collection of Sample in Bags

7.4.1 Assemble a sample collection system such as the one shown in Figure 2. Use only bags that have been cleaned and checked according to Section 7.3.

7.4.2 Start pumps and allow them to warm up for 15 minutes. Then check flow rate for proper value to fill bag over the required time period (see Section 6.2).

7.4.3 Fill bags; keep them away from heat and sunlight during sampling and transporting.

7.4.4 Analyze bag samples within 3 hours.

7.5 Analysis Procedure

7.5.1 Assemble the analysis system as shown in Figures 1 and 4 and as discussed in Section 6. Allow the FID analyzer to warm up and stabilize for several hours before analysis.

7.5.2 Check and adjust helium pressure to provide a flow rate of 76 cm^3/min.

7.5.3 Close valve V2 and open valve V1 to evacuate the vacuum reservoir.

7.5.4 Place the six-port valve in the inject position.

7.5.5 Open valve V2 and adjust valve V3 for a sample flow of 45 to 60 cm^3/min.

7.5.6 Connect sample canister, bag, or direct sample inlet to port five of the six-port valve as shown in Figure 1. For a canister, open the canister valve and adjust valve V4 to obtain a slight vent flow as indicated by constant bubbles. (CAUTION: Do not allow water to be drawn into the six-port valve.) Then close valve V2. Also, significantly better recovery of aromatics from a canister can be obtained by heating the canister to about 80° C with heating tape or a heated enclosure.

7.5.7 Open valve V1 to evacuate the vacuum reservoir. With the six-port valve in the inject position and valve V1 open, open valve V2 for a few minutes to flush and condition the inlet lines. Close valve V2.

7.5.8 Submerge the trap in the cryogen and check and maintain the cryogen level constant so that it completely covers the coils of the trap (same level used during calibration). Allow a few minutes for the trap to cool completely.

7.5.9 With the six-port valve still in the inject position, close valve V1 and open valve V2.

7.5.10 Observe the increasing pressure on the pressure gauge; when it reaches an arbitrary point such as 20 mm Hg, quickly switch the six-port valve to the sample position.

7.5.11 Observe the increasing pressure on the pressure gauge; when it reaches a second arbitrary point such as 200 mm Hg, quickly switch the valve to the inject position, keeping the cryogenic bath on the trap. Close valve V2 to conserve the remaining sample in the canister or bag.

7.5.12 Start the chart recorder, and wait until the response baseline has stabilized (about 3 to 5 minutes). Do not wait longer than 7 minutes.

7.5.13 Start the integrator. Remove the liquid cryogenic bath and smoothly but not too quickly replace it with a Dewar of hot water (approximately 80° C). Use the same level of hot water for both calibration and sample analyses. Placing the hot water on too quickly may cause an initial negative-going response which could hamper accurate integration.

7.5.14 Observe the response peak. Determine the total NMOC integrated peak area and use the calibration curve to convert the reading into concentration units (ppbC). Note that the NMOC peak shape may not be reproducible due to differences in placing the hot water on the trap, but the total NMOC peak area should be reproducible.

7.5.15 Blot the trap dry. If analyzing a bag or canister, repeat the analysis two or three times and report the average NMOC concentration.

8. CALIBRATION

8.1 Calibration Frequency

Initially a complete dynamic calibration of five or more points should be carried out on each range to define the calibration curve. Subsequently, the calibration should be verified with two- or three-point calibration checks (including zero) two or three times per week or each time the analytical system is restarted after being shut down.

8.2 Calibration Standards

Propane calibration standards may be obtained directly from low-concentration cylinder standards or by dilution of high-concentration cylinder standards with zero air. Dilution flow rates must be measured accurately, and the combined gas stream must be mixed thoroughly. Calibration standards may be sampled directly from the flowing stream, or sample bags or canisters may be filled and analyzed. Remember that propane concentrations in ppmC are three times the volumetric concentration in ppm.

8.3 Calibration Procedure

8.3.1 Select one or more combinations of FID analyzer attenuator setting, output voltage setting, integrator resolution (if applicable), and sample volume to provide the desired range or ranges (e.g., 0-500 ppbC or 0-5000 ppbC). Each such range should be calibrated individually and have a separate calibration curve.

8.3.2 Analyze each calibration standard three times according to the procedure in Section 7.5. Be sure that flow rates, liquid level in the Dewars, timing, and other variables are the same as will be used during analysis of ambient samples.

8.3.3 Average the three results for each concentration standard and plot the calibration curve(s) as integrator peak area reading versus concentration in ppbC. Linearity should be expected, at least about 150 ppbC. Points that appear to deviate abnormally should be repeated. Relative standard deviation for the three analyses should be less than 5 percent. If nonlinearity is observed at low concentrations, additional points in that region may be needed to adequately define the calibration curve.

9. METHOD MODIFICATIONS

9.1 Sample Metering System

Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume is efficient and convenient, other techniques should work also. For example, a constant sample flow could be established with a vacuum pump and a critical orifice, with the six-port valve being switched to the sample position for a measured time period. Or a gas volume meter such as a wet test meter could be used to measure the total volume of sample air. However, these alternate techniques have not been tested or evaluated.

9.2 TOC Analyzer

FID analyzers other than the Beckman model 400 specified may also be adaptable to the method. The specific flow rates and necessary modifications for the helium carrier for any alternate FID would have to be worked out by the user.

9.3 Range

It may be possible to increase the sensitivity of the method by increasing the sample volume. However, other limitations are likely to

arise; hence any attempts to increase the sensitivity should be tested carefully.

9.4 Alternate Carrier Gas

It may be possible to substitute nitrogen for the helium carrier, but no tests using a nitrogen carrier have been carried out.

9.5 Nonlinear Calibration

Although FID response is usually linear, tests during method development produced a nonlinear calibration below 150 ppbC.[5] No explanation for this is apparent. It may be possible to adjust the sample volume, FID attenuation, or integrator resolution to reduce this nonlinearity.

9.6 Trap Heating

Other techniques may be used for heating the trap during the analysis phase. For example, with a suitable temperature control, the trap could be heated electrically by passing electrical current directly through the trap tubing, heating the trap using its internal resistance.

10. REFERENCES

1. Uses, Limitations and Technical Basis of Procedures for Quantifying Relationships Between Photochemical Oxidants and Precursors. EPA-450/2-77-021a, U.S. Environmental Protection Agency, Research Triangle Park, NC, November 1977.

2. Guidance for Collection of Ambient Non-Methane Organic Compound (NMOC) Data for Use in 1982 Ozone SIP Development, and Network Design and Siting Criteria for the NMOC and NO_x Monitors. EPA-450/4-80-011, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1980.

3. Guidance for the Collection and Use of Ambient Hydrocarbon Species Data in Development of Ozone Control Strategies. EPA-450/4-80-008, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1980.

4. Sexton, F. W., McElroy, F. W., Michie, R. A., Jr., Thompson, V. L., A Comparative Evaluation of Seven Automatic Ambient Non-Methane Organic Compound Analyzers. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC (Draft document).

5. Laboratory Evaluation of Non-Methane Organic Carbon (NMOC) Determination by Cryogenic Preconcentration and Flame Ionization Detection, Draft Report, Research Triangle Institute, March 1981.

6. Collection and Analysis of Non-Methane Hydrocarbon Transport Data From Upwind Ozone Monitoring Sites for Louisville, Kentucky and Nashville, Tennessee. EPA-904/9-80-055, U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1981.

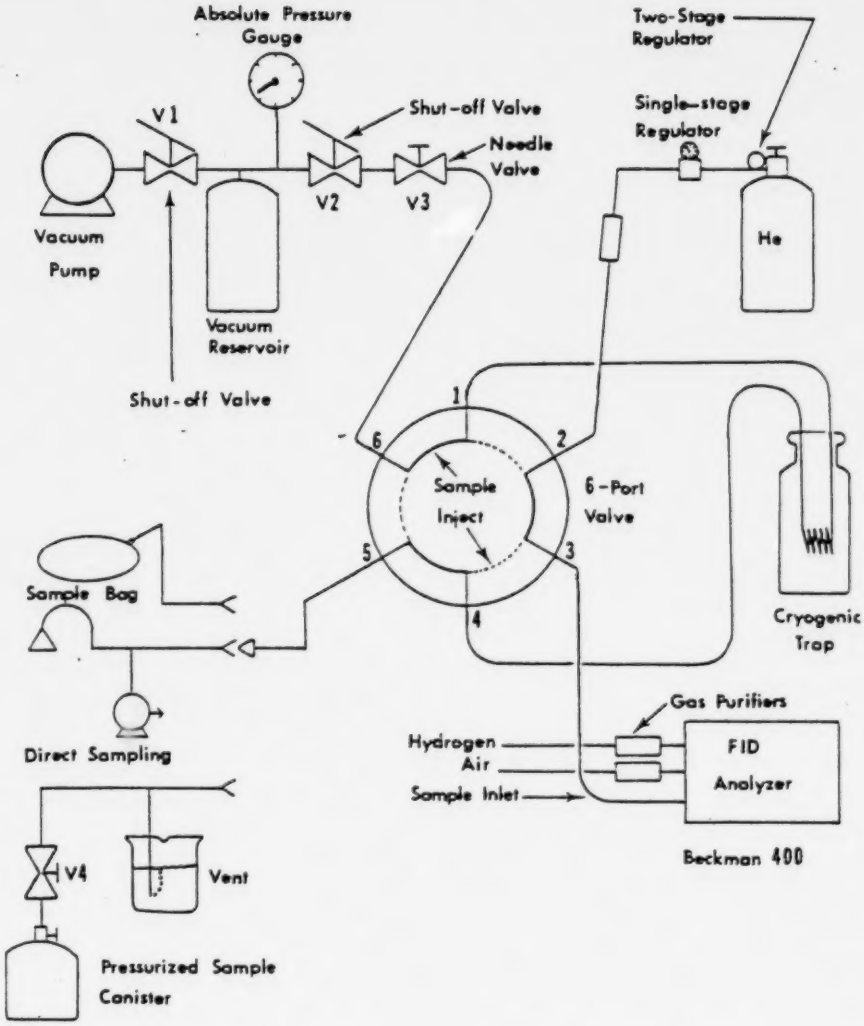

Figure 1. Schematic of analysis system showing three sampling modes.

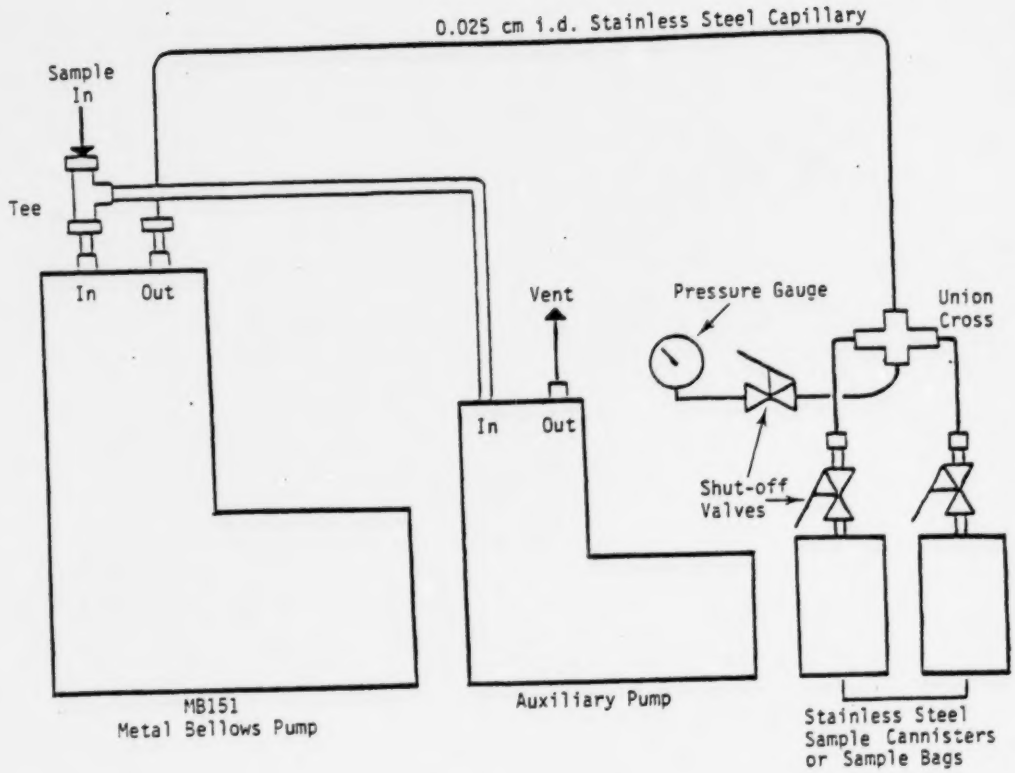

Figure 2. Sample system for collection of integrated field samples.

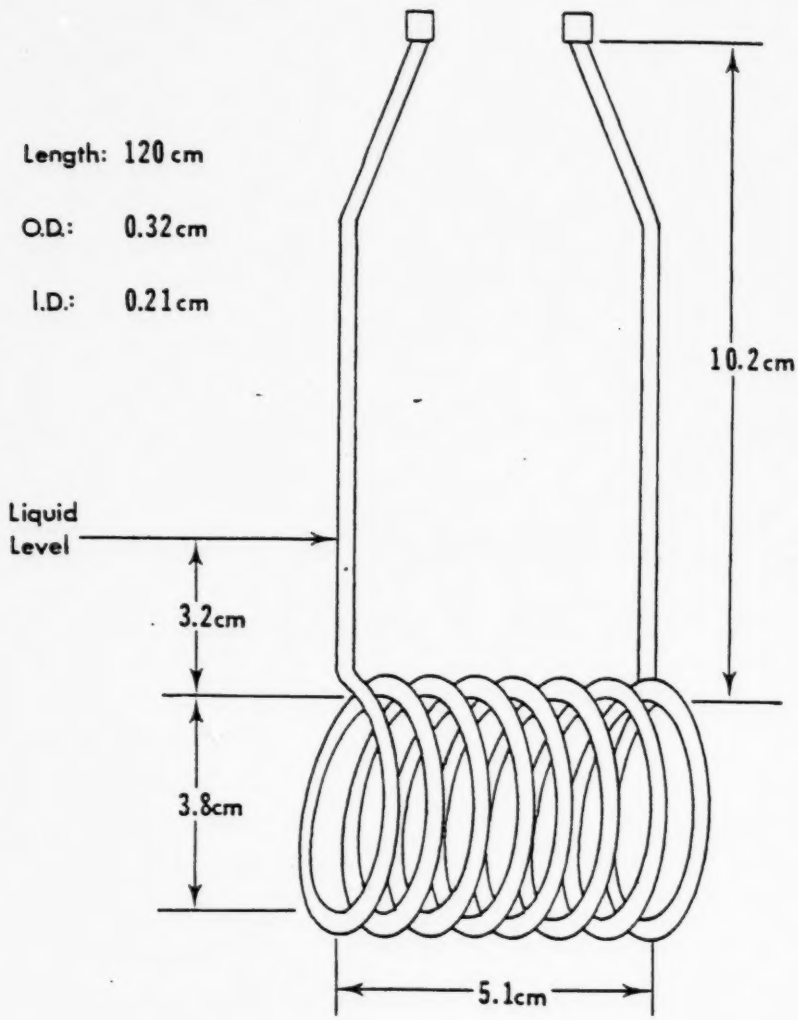

Figure 3. Sample trap dimensions.

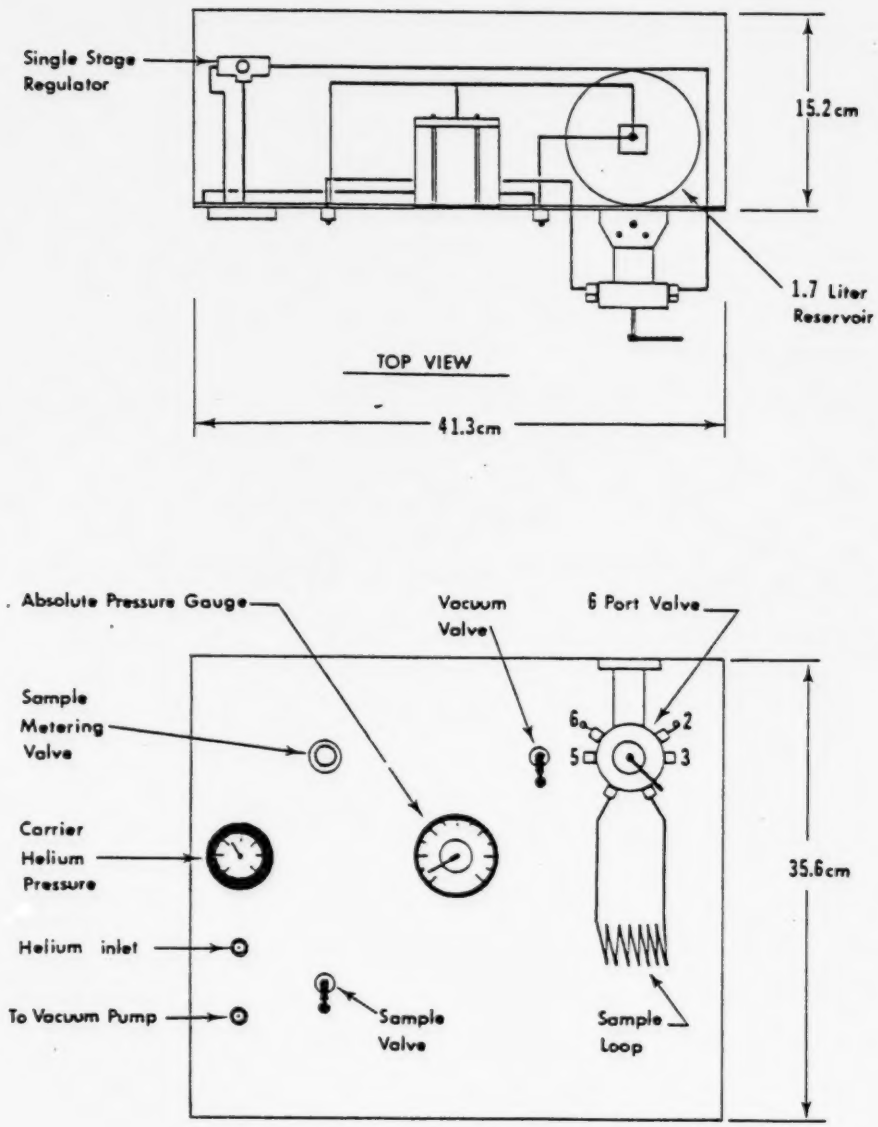

Figure 4. A modular design for the analysis system.

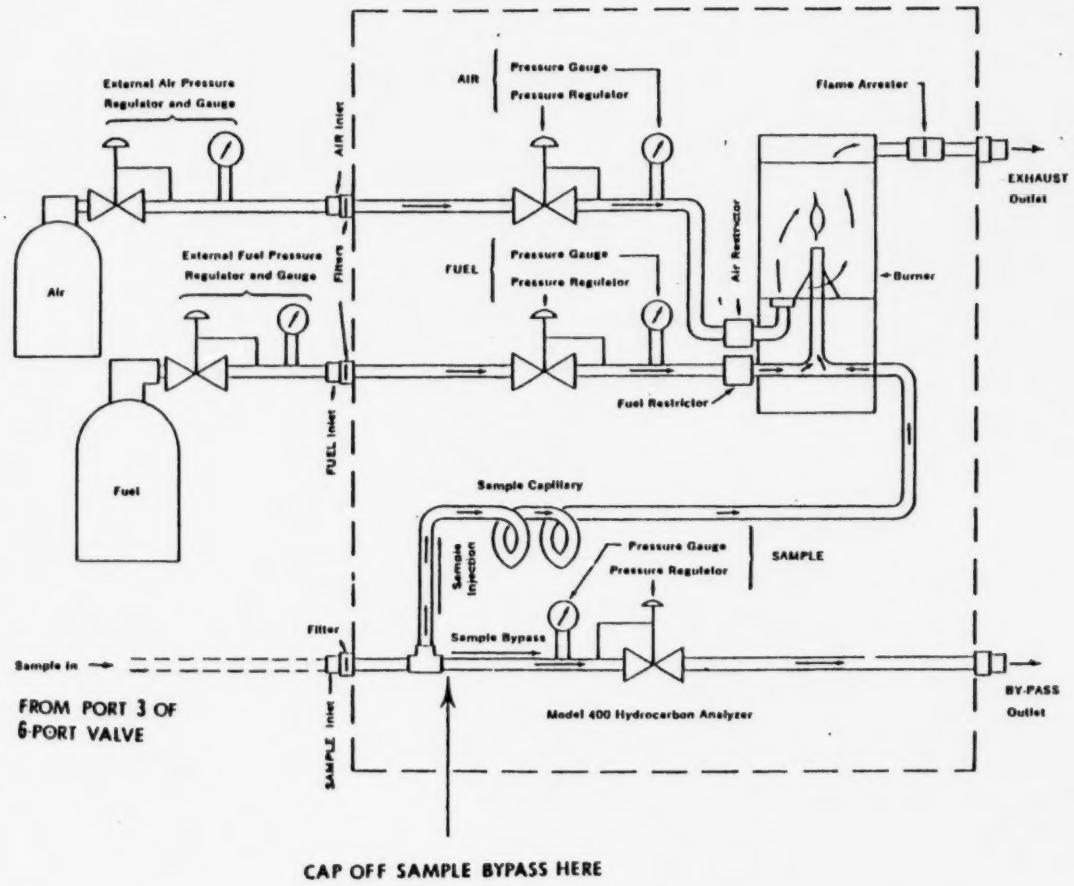

Figure 5. Schematic of Beckman 400 hydrocarbon analyzer showing modification.

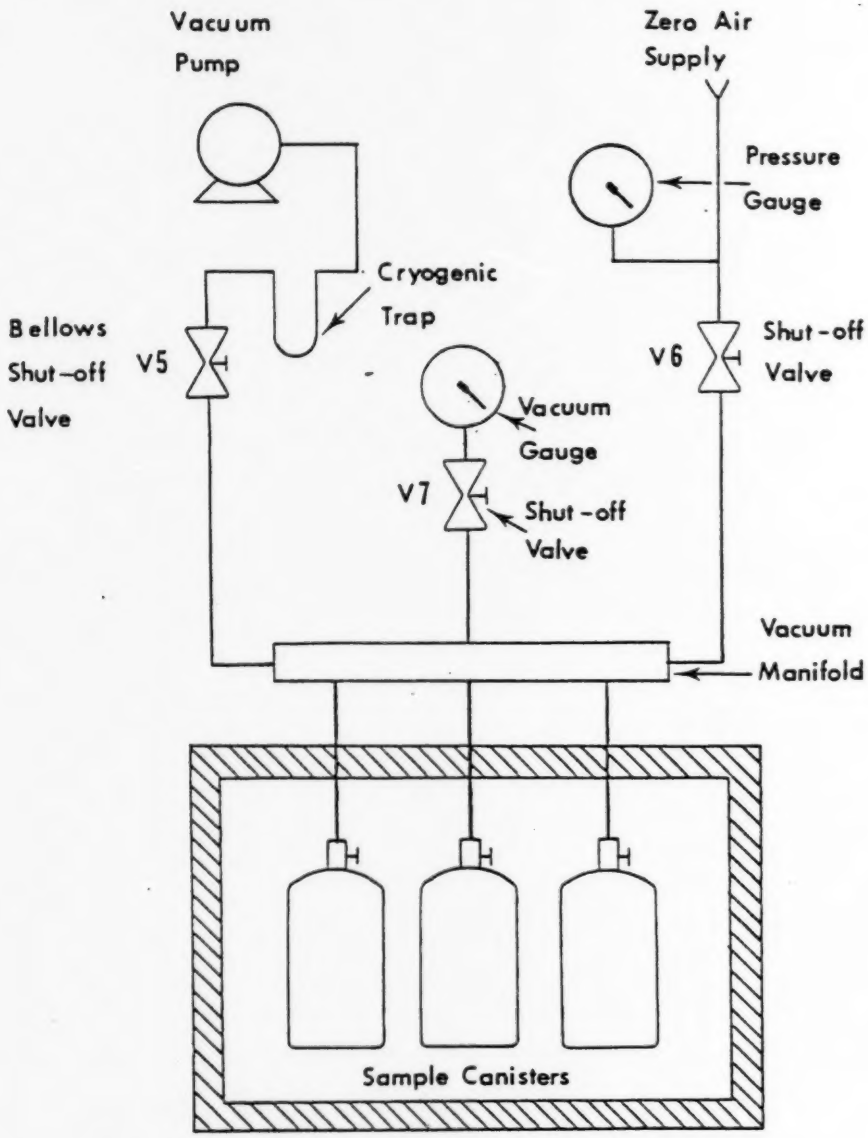

Figure 6. Canister cleaning system.

APPENDIX

MATERIAL	MODEL/DIMENSIONS	SUPPLIER
1. Sample Canister	4-6 Liter	D&S Instruments, Ltd. N. 1218C Grand Ave. Pullman, WA 99163 (509) 332-3684
2. Absolute Pressure Gauge	Model 61D-ID-0200, (0-200 mm Hg), 2-1/2 in. Face	Wallace & Tiernan Div. of Pennwalt Corp. 25 Main Street Belleville, NJ 07109
3. Six-Port Valve	Valco 9110	Alltech Associates 606A Union Street Kenneth Square, PA 19348
4. Gas Purifiers	Cat #8125	Alltech Associates
5. Chromatographic Grade Stainless Steel Tubing	Cat #30101 (1/8 in. × 0.085 in.)	Alltech Associates
6. Integrating Chart Recorder	Linear Model 252A	Cole-Parmer 7425 North Oak Avenue Chicago, IL 60648
7. Tedlar sampling bags	Catalog No. 1409	Horizon Ecology Company 7435 N. Oak Park Avenue Chicago, IL 60648
8. FID TOC Analyzer	Beckman Model 400	Beckman Instruments, Inc. Process Instruments Div. 2500 Harbor Boulevard Fullerton, CA 92634
9. Aluminum suitcase		Zero Corporation 777 Front Street Burbank, CA 91503
10. Metal Bellows pump	Model MB-151	Metal Bellows Corporation 1075 Providence Highway Sharon, MA 02067
11. Vacuum gauge	$0\text{-}10^{-3}$ mm Hg	Consolidated Vacuum Corporation
12. Cryogenic Dewar	10-196-10B (30 cm × 26 cm)	Fisher Scientific Company